

PATENT SPECIFICATION

NO DRAWINGS

1.061.161



1.061.161

Date of Application and filing Complete Specification: Feb. 14, 1964.
No. 6288/64.

Application made in United States of America (No. 284019) on May 29, 1963.

Complete Specification Published: March 8, 1967.

© Crown Copyright 1967.

Index at acceptance:—C1 A(H11G, H11L, H11X, H12C, H12X, H13); C5 G1A1

Int. Cl.:—C 10 I 1/10//C 10 g

COMPLETE SPECIFICATION

Fuel Oil Additives

We, BASIC INCORPORATED, a Corporation organised and existing under the laws of the State of Ohio, United States of America, of 845 Hanna Building, Cleveland, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to fuel oil additives in the form of concentrates containing solid particulate metal-containing compounds effective as corrosion inhibitors dispersed in an organic distillate fuel oil.

Many combustible organic liquids, such as residual fuel oils, and solid fuels, such as coal and coke, contain corrosive compounds exemplified by vanadium and/or sulphur compounds which attack metal, particularly upon combustion of the fuel leaving a corrosive ash. Combustion of sulphur-bearing fuels yields acidic flue gases or sulphuric acid which attack preheaters, economizers, stacks and flue liners.

It has been suggested to use minor amounts of corrosion-inhibitors in fuels to counteract such corrosive action. For example, organometallic fluids, for instance magnesium alkyl aryl sulphonate, can be prepared by chemical reactions, or by dissolving solid organometallic compounds in organic solvents. But in all of such cases the weight fraction of metal present in the final fluid is limited by the ratio of the atomic weight of the metal to the molecular weight of the compounds and/or by the solubilities of such compounds in the solvents. The metal content of emulsions of water soluble salts is also restricted to quite low levels by a combination of the solubility limits of the salt in water and also by the proportion of the aqueous phase which can be incorporated into a stable emulsion. Thus, in all presently known systems, there is a definite relatively low limit on the amount of

[Price 4s. 6d.]

a metal-containing corrosion-inhibitor which can be incorporated in a fuel oil without sacrificing fluid characteristics.

For reasons of economics and ease of use, it will obviously be highly desirable to increase the loading of a metal-containing compound in an oil concentrate, adapted to be added to a fuel composition, without adversely affecting the physical characteristics of the concentrate. For instance, the concentrate must be stable even though containing appreciable quantities of the metal additive and, further, must be pumpable so that the concentrate may be readily added to fuel being sent through lines to a main body of a fuel composition as to a burner of a furnace, boiler or turbine. Normally, heavily loaded slurries sufficiently lose fluid properties to prevent circulation of the slurry and even grinding of its solid component as by ball mills.

In accordance with the present invention it has now been found that the amount of metal-containing corrosion inhibitor that can be loaded into an organic fuel oil can be very materially increased by adding as a dispersing agent an oil-compatible carboxylic acid or carboxylic acid salt. Accordingly, there is now provided a concentrate suitable for addition to a fuel oil containing corrosive elements to provide therein a metal-containing corrosion inhibitor, said concentrate being a fluid, pumpable dispersion at room temperature and comprising an organic distillate fuel oil having dispersed therein at least 40% by weight based on the total weight of the dispersion, of a solid particulate metal-containing compound which is active as a corrosion inhibitor against said corrosive elements, and, as a dispersant for said particulate compound, an oil-compatible (as hereinafter defined) carboxylic acid or carboxylic acid salt.

The solids that are incorporated into the liquid fuel oil in accordance with the invention are particulate metal containing com-

Price 75p

pounds effective as corrosion inhibitors. Particularly suitable compounds are the compounds of magnesium, aluminium, calcium, manganese, thorium, sodium, potassium, barium, zinc, strontium, and the rare earth metals. Such compounds include the oxides, hydroxides, acetates, carbonates, silicates, oxalates, sulphates, nitrates and halides of such metals. Naturally occurring ores such as magnesite, brucite, dolomite, and talc may also be used. Magnesia is preferred, and especially magnesia in the form of calcined brucite. Brucite is easy to grind and the soapy, flaky nature of the resulting product lends itself to an even more stable suspension. Calcined brucite presents a relatively long, narrow, flat sheet form rather than a spherical shape. This sheet form resists settling of the suspension.

The distillate fuel oil forming the carrier liquid may notably comprise the variously known distillate fuel compositions, since the concentrate is ultimately added to a fuel. Typical distillate fuel oils suitable as carrier liquids include diesel fuels, heating oils and petroleum fuels.

By the term 'oil-compatible carboxylic acid or carboxylic acid salt' is meant such an acid or salt that is readily dispersible in, and preferably substantially miscible with, the organic liquid forming the carrier of the concentrate, such as those oils previously noted, in the presence of the solids content. Exemplary of these acids are tall oil acids, rosin acids (principally abietic acid), hydrogenated rosin acids, aromatic and alkyl-aromatic acids such as benzoic acid and methyl benzoic acid, naphthenic acids, and the fatty acids. The lower molecular weight fatty acids such as acetic may not be oil-miscible by themselves but have been found to be oil-miscible in the presence of solids, for example magnesia. Accordingly, such lower molecular weight fatty acids including formic acid are operable and within the contemplation of the invention.

In the preferred practice of the invention, however, the acids are substantially water-insoluble and oil-miscible (even in the absence of the solids component) such as those acids first mentioned. Accordingly, the relatively higher molecular weight fatty acids of the fatty acid series are employed in the preferred practice and chiefly those fatty acids normally considered to be soap-producing. In general, however, a desired fatty acid may be one having 5 to 20 carbon atoms within the broader operable range of 1 to 20 carbon atoms. The fatty acids may be either saturated or unsaturated. For example desirably fatty acids that may be used include caproic, 2-ethylhexanoic, lauric, myristic, pentadecanoic, palmitic, margaric, linolenic, oleic, ricinoleic, and stearic acids as well as mixtures thereof. Also, Tallene (a by-product recoverable from waste paper liquors which comprises a mixture of fatty and rosin acids) may be used.

Obviously, proportions are not critical. The objective is to incorporate into the carrier liquid of the concentrate as much as possible of the solids. Any addition of the oil-compatible acid component tends to increase the permissive load of the solids. As an example, an addition of 0.5 per cent to 15 per cent by weight of the acid component, based on the weight of the concentrate, enables from 40 per cent to 85 per cent by weight of solids to be incorporated in the oil of the concentrate while retaining stable and pumpable physical characteristics.

To prepare the present stable concentrate, the solids component is comminuted and then mixed in any order with the fuel and dispersing agent. The degree of comminution is not critical, although the finer the particles the more easily they are dispersed. Fine particles having sizes of 2 to 10 microns and preferably of 2 to 4 microns produce good results. While a fine particle size is desirable, a particulate material passing only 80 per cent through a 150 mesh, U.S. Standard Sieve, has been used to prepare uniform and stable dispersions which flow readily at room temperature. Even coarser particle sizes can be used, for example, 80 per cent of a particulate material passing a 100 mesh, U.S. Standard Sieve.

Normally, fine particle size materials require greater quantities of the acid or dispersing agent per weight unit of solids to obtain a given fluidity than do coarse materials. For a given particles size, the solids content of the concentrate or suspension can be increased at the expense of the suspending medium with a minimum of sacrifice of solid properties by simultaneously increasing the amount of the dispersing agent. The proportions to be employed may be determined by balancing particle size requirements and the economic value of higher loadings against adverse effects on handling characteristics, pour point and viscosity. Solids contents of up to 84 per cent by weight have been prepared using as little as 0.76 per cent by weight dispersant, the balance being a fuel oil. Dispersant or acid concentrations beyond about 15 per cent by weight of the concentrate, although operable, appear to provide little gain in fluidity and are usually not economically justified. The comminution can be carried out by conventional milling means, wet or dry, such as by ball, rod, tube, colloid, roller, vibrating or jet mills. The comminution and blending can be carried out simultaneously.

As increasing quantities of a ground metal-containing compound such as magnesia and fuel oil are mixed, a heavy grease-like mixture normally results which cannot be pumped or blended as desired. This, however, does not occur where the present dispersant is used. In many instances, as in the case of magnesia, there may be a chemical reaction between the

metal-containing corrosion-inhibitor and the oil-compatible acid component. Stoichiometric reaction between these two reactants renders any unreacted portion of the metal compound completely dispersible and reduces the viscosity of the mixture substantially. The reaction may be regarded as producing, for instance in the case of magnesia, a magnesium soap which is soluble in the fuel oil and acts as a surface active agent which promotes the dispersion of the solid metal-containing material in the fuel oil to form a stable mixture.

In this regard it will be noted that oil-compatible salts or like compounds of the acid component including metal salts and fatty amines may at times be added directly to the concentrate dispersion in lieu of relying on the acid alone or on a reaction between the metal compound and acid to produce the salt or other reaction product. Accordingly, the appended claims are to be construed as encompassing also any such salt, where applicable, whether the salt or other compound is formed in situ or is added directly as the salt or like compound.

In one instance, a distillate fuel oil dispersion containing 40 per cent by weight of magnesia was non-pumpable and, for all practical purposes, a solid. When treated in accordance with the present invention by addition of oleic acid, the mixture not only became a stable fluid dispersion and pumpable, but an additional 30 per cent by weight of magnesia (making a total percentage of 70 per cent) could be added. The concentrate so prepared had not appreciably settled after several weeks.

Such an increase in loading of magnesia or like component also permits significant increases in solids throughput for a grinding operation such as a homogenizer and, further, considerably reduces unit power cost. For example, assuming a solid and a liquid with specific gravities of 2.4 and 0.85, respectively, increasing the solids concentration by the present invention from 40 per cent to 70 per cent results in an increase in solids throughput per gallon from approximately 3.8 to 9.0 pounds. Since power consumption is fixed, a reduction in power cost per unit to less than half of that at 40 per cent is thereby achieved.

It is recognised that a metal-containing corrosion-inhibitor may be added in one form and changed to another due to attendant conditions. For example, milling magnesia with fuel oil in the presence of water may convert the former to the hydroxide.

To prepare the concentrate, the ingredients are mixed in any order, although usually the dispersing agent is mixed with the suspending fuel and the metal compound then added. The fuel oils to which the concentrate may be added (as contrasted with the fuel of the concentrate itself) may be any of those known

in the art, such as diesel fuel, heating oils, and petroleum fuels, which contain corrosive compounds such as those of sulphur and/or vanadium. The concentrates are especially suitable for addition to residual fuel oils typified by No. 5, No. 6, and Bunker "C" fuel oils which contain vanadium or sulphur or other like constituents which may produce a corrosive ash or vapor upon combustion of the fuel. These residual fuel oils are the residues obtained from conventional distillation of crude oils, from the thermal cracking, of topped crudes, and from heavy petroleum residues which have had their viscosity reduced by known means, e.g. by dilution with distillate fuel oil stocks.

The concentrate can be added to the fuel by various techniques, such as by mixing the concentrate with the fuel by addition to a small day tank, or by mixing the concentrates into the fuel flowing to a burner, or by separate injection of the concentrate into a combustion chamber. In general, the method of adding the concentrate is dependent on the nature of the fuel and the particular equipment employed.

The quantity of concentrate or additive used is primarily governed by the amount of corrosive agent present in the fuel, by the presence or absence of sulphur, and by whether or not combustion conditions result in the conversion of sulphur to sulphuric acid. Also, although in every case a sufficient amount of the concentrate could be employed to inhibit the action of all corrosive agents, in practice a quantity is apt to be used which is sufficient only to reduce corrosion to a tolerable level and to meet air pollution restrictions on stack emission.

In order to demonstrate the invention, the following examples are set forth for the purpose of illustration only. Any specific enumeration or detail mentioned should not be interpreted as a limitation of the invention unless specified as such in one or more of the appended claims and then only in such claim or claims.

EXAMPLE 1

The following ingredients in the proportions by weight indicated were milled together in a vibrating mill:

Calcined brucite	55%	
No. 1 fuel oil	35%	
Tallene	10%	120

This concentrate was quite stable over five weeks with a minimum of settling at that time and was fluid and pumpable. The concentrate was later added to a residual fuel oil for use in an oil-fired furnace.

Settling tests at the conclusion of five weeks for this concentrate made at room temperature (70°F--75°F) showed a one per cent increase in solids in the bottom 10 per cent

of the sample as compared to a 3.5 per cent decrease in the top 10 per cent sample.

EXAMPLE 2

5 Dolomite in an amount of 300 grams was added to 150 grams of No. 2 fuel oil in a Waring blender. There resulted a non-fluid paste containing 66.6 per cent solids. Addition of 1 gram of tallen converted the mix to an extremely fluid and pumpable dispersion.

10 In the foregoing examples, Tallene was used because of its low cost and ready availability. In lieu thereof the other oil-compatible acids previously disclosed could have been used. The No. 1 and No. 2 fuel oils used in the
15 Examples are commercially available distillate oils, see Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 10, (1953), pages 165 and 166.

WHAT WE CLAIM IS:—

20 1. A concentrate suitable for addition to a fuel oil containing corrosive elements to provide therein a metal-containing corrosion inhibitor, said concentrate being a fluid, pumpable dispersion at room temperature and comprising an organic distillate fuel oil having dispersed therein at least 40% by weight,
25 based on the total weight of the dispersion, of a solid particulate metal-containing compound which is active as a corrosion inhibitor against said corrosive elements, and, as a dispersant for said particulate compound, an oil-compatible (as hereinbefore defined) carboxylic acid or carboxylic acid salt.

30 2. A concentrate according to claim 1, in which the dispersant is a tall oil acid, resin acid, hydrogenated rosin acid, benzoic acid, methyl benzoic acid, naphthenic acid, a fatty acid containing from 1—20 carbon atoms, or a salt of any one of said acids.

40 3. A concentrate according to claim 2, in

which the dispersant is a fatty acid containing from 5—20 carbon atoms.

4. A concentrate according to claim 1, in which the dispersant is a soap-producing fatty acid. 45

5. A concentrate according to any one of the preceding claims, which contains from 0.5—15% by weight of the dispersant based on the weight of the composition.

6. A concentrate according to any one of the preceding claims, which contains from 40—85% by weight of the particulate solid. 50

7. A concentrate according to any one of the preceding claims, in which the particulate solid is an inorganic compound of magnesium, aluminium, calcium, manganese, thorium, sodium, potassium, barium, zinc, strontium or a rare earth metal. 55

8. A concentrate according to claim 7, in which the particulate solid is magnesia. 60

9. A concentrate according to claim 7, in which the particulate solid is magnesium hydroxide.

10. A concentrate according to claim 7, in which the particulate solid comprises soaplike flakes of calcined brucite. 65

11. A concentrate according to any one of the preceding claims, in which the particulate solid has a particle size in the range 2—10 microns. 70

12. A concentrate according to claim 11 in which the particulate solid has a particle size in the range 2—4 microns.

13. Concentrates according to claim 1, being concentrates substantially as hereinbefore described in either of the Examples. 75

For the Applicants,
D. YOUNG & CO.,
Chartered Patent Agents,
9 Staple Inn,
London, W.C.1.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1967.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained